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CHEMISTRY

Thiophene and Naphthalene Eutectics with Benzene Homologs

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Abstract—The variation in composition and melting point of binary eutectics of thiophene and naphthalene with benzene homologs is established. Analysis permits prediction that eutectics will exist in 48 binary systems and 67 ternary systems that have not been experimentally studied.

Keywords: thiophene, naphthalene, benzene homologs, liquid–solid equilibrium, binary eutectics

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The liquid–solid equilibrium in systems formed by thiophene and naphthalene with coal-tar components was investigated experimentally in [1, 2] (Table 1). These are binary systems of thiophene with benzene homologs and of naphthalene with benzene homologs.

Available data allow us to consider two series of liquid–solid binary systems: thiophene + benzene homologs; and naphthalene + benzene homologs. We may analyze the relations between the melting point of the eutectic mixture and the melting point of the variable component in the homologous series and between the melting point of the eutectic mixture and the content of the constant component in the homologous series.

For the series consisting of thiophene + benzene homologs, the dependences of the melting point of the eutectic mixture on the melting point of the benzene homolog and on the content of the constant component in the homologous series (thiophene) are approximately logarithmic and linear, respectively.

The equations in Table 2 describe the dependence of the melting point T_{eut} of the eutectic mixture on the melting point T_h of the variable component in the

Table 1. Experimental data [1, 2]

System	Melting point of the eutectic mixture T_{eut}, °C	Content of thiophene (naphthalene) in eutectic, mol %	Melting point of the variable component in the series T_{comp}, °C	Source
Thiophene (–38.2)–benzene homologs				
Thiophene–benzene	Not formed		5.5	[1]
Thiophene–1,3-dimethylbenzene	–80.0	62.1	–47.8	
Thiophene–ethylbenzene	–107.0	40.6	–94.4	
Thiophene–methylbenzene	–111.0	37.1	–95	
Naphthalene (80.29)–benzene homologs				
Naphthalene–1,4-dimethylbenzene	4.2	18.2	13.26	[2]
Naphthalene–benzene	–3.6	13.4	5.5	
Naphthalene–1,2-dimethylbenzene	–28.0	6.6	–25.18	
Naphthalene–1,3-dimethylbenzene	–49.0	3.7	–47.8	
Naphthalene–ethylbenzene	–95.0	1.74	–94.4	
Naphthalene–methylbenzene	–96.0	2.18	–95	

Table 2. Equations for thiophene + benzene homologs

Series	Equation	Determination coefficient
Thiophene–benzene homologs	T_{eut}=61.23ln$x$–332.95	0.9979
	$T_{eut} = 0.6191T_h - 50.385$	0.9884

homologous series and the dependence of T_{eut} on the thiophene content x (mol %).

Analysis of these equations permits prediction of the existence of eutectic mixtures in 21 binary systems of the series consisting of thiophene + benzene homologs that have not been experimentally investigated, with benzene homologs whose melting point is between –95 and –47.8°C (Table 3).

For the series consisting of thiophene + benzene homologs, the experimental dependences of the melting point of the eutectic mixture on the melting point of the benzene homolog and on the content of the constant component in the homologous series (naph-

Table 3

Variable component in the homologous series with thiophene (T_h, °C)*	Properties of the eutectic**	
	T_{eut}, °C	thiophene content x, mol %
Propylbenzene (–99.5)	–111	37
Butylbenzene (–87.99)	–104	41
1-Butyl-4-methylbenzene (–85.0)	–103	42.7
1,3-Dimethyl-5-ethylbenzene (–84.33)	–102.6	43
1,3-Diethylbenzene (–83.92)	–102.3	43
Sec-butylbenzene (–75.49)	–97	47.0
1-Pentylbenzene (–75)	–96.8	47.3
1-Isopropyl-2-methylbenzene (–71.54)	–94	49
1-Isopropyl-4-methylbenzene (–67.94)	–92.4	50.8
1,2-Dimethyl-4-ethylbenzene (–67.0)	–91.9	51.3
1,3,5-Triethylbenzene (–66.5)	–91.5	51.5
1-Isopropyl-3-methylbenzene (–63.75)	–89.8	53.0
1,3-Diisopropylbenzene (–63.1)	–89.5	53.3
2,4-Dimethyl-1-ethylbenzene (–63.0)	–89.4	53.4
Tret-butylbenzene (–57.86)	–86	56.2
1,2-Diisopropylbenzene (–56.7)	–85	56.9
1,4-Dimethyl-2-ethylbenzene (–53.7)	–83.6	58.7
1-*Tret*-butyl-2-methylbenzene (–52.52)	–82.9	59.4
Isobutylbenzene (–51.52)	–82.31	59.9
1-*Tret*-butyl-2-methylbenzene (–50.32)	–81.5	60.7
1,2-Dimethyl-3-ethylbenzene (–49.5)	–81.0	61

* The melting points of the benzene homologs are taken from [3].

** Decimal values are shown only to illustrate the trends in the eutectic melting point and the content of the variable component in the homologous series in the eutectic with similar melting points of the benzene homologs.

Table 4. Equations for naphthalene + benzene homologs

Series	Equation	Determination coefficient
Naphthalene–benzene homologs	$T_{eut} = 44.724 \ln x - 119.29$	0.9623
	$T_{eut} = -0.0013 T_h^2 + 0.8149 T_h - 7.0764$	0.9998

thalene) are approximately logarithmic and exponential, respectively.

The equations in Table 4 describe the dependence of the melting point T_{eut} of the eutectic mixture on the melting point T_h of the variable component in the homologous series and the dependence of T_{eut} on the naphthalene content x (mol %).

Analysis of these equations permits prediction of the existence of eutectic mixtures in 27 binary systems of the series consisting of naphthalene + benzene homologs that have not been experimentally investigated, with benzene homologs whose melting point is between –99.5 and –6.25°C (Table 5).

Experimental and calculated results for ternary eutectic systems formed by naphthalene and benzene homologs were also presented in [2]. Experiments showed the existence of ternary eutectics in eight ternary systems. The parameters of ternary eutectics were calculated for 35 ternary systems in conditions where their behavior is ideal. The agreement of the calculated and experimental results was satisfactory.

To construct series of eutectics, we require data for at least three systems in which two components are constant and the third is variable (a member of the chosen homologous system). For three series containing naphthalene, such data were given in [2] (Figs. 1 and 2):

—naphthalene + 1,2-dimethylbenzene + benzene homologs (1,3-dimethylbenzene, ethylbenzene, methylbenzene);

—naphthalene + 1,4-dimethylbenzene + benzene homologs (benzene, 1,2-dimethylbenzene, 1,3-dimethylbenzene, ethylbenzene, methylbenzene);

—naphthalene + benzene + benzene homologs (1,2-dimethylbenzene, 1,3-dimethylbenzene, ethylbenzene, methylbenzene).

Analysis of the data on ternary eutectic systems allows us to add to the list of such systems formed by naphthalene and benzene homologs (Table 6). For the series consisting of naphthalene + 1,2-dimethylbenzene + benzene homologs, ternary eutectics are formed in systems with benzene homologs whose melting point is between –47.8 and –95°C. For the series consisting of naphthalene + 1,4-dimethylbenzene + benzene homologs, ternary eutectics are formed in systems with benzene homologs whose melting point is between +5.5 and –95°C. For the series consisting of naphthalene + benzene + benzene homologs, ternary eutectics are formed in systems with benzene homologs whose melting point is between –25.8 and –95°C.

Organizing experimental data into series of liquid–solid systems permits prediction of the behavior of systems with other homologs in the series (both qualitatively and quantitatively) and thus reduces experimen-

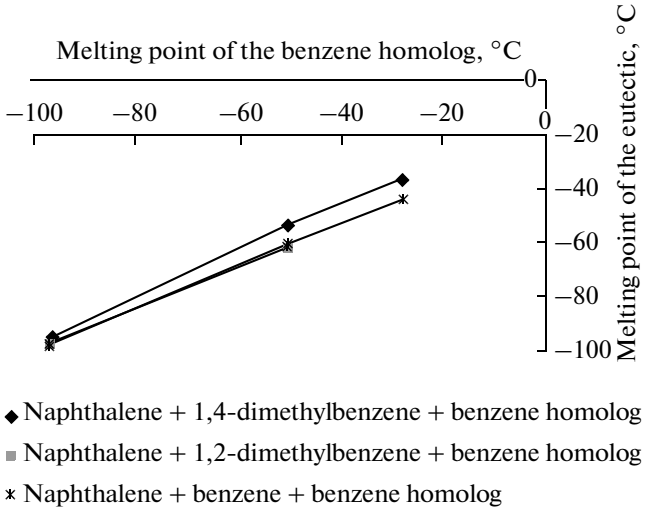

Fig. 1. Dependence of the melting point of the eutectic mixture on the melting point of the benzene homolog for ternary systems.

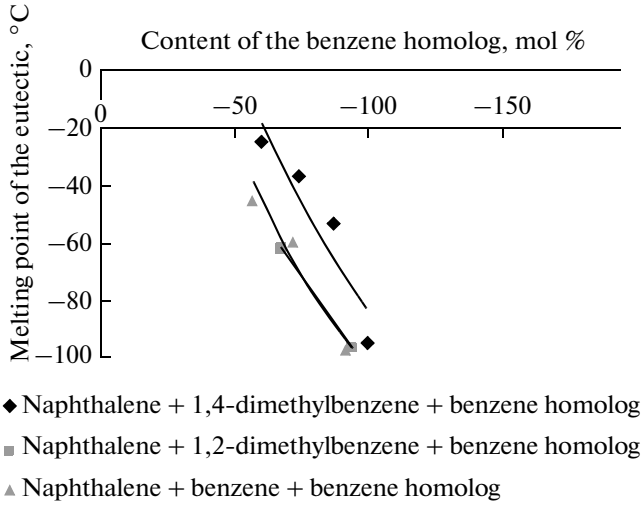

Fig. 2. Dependence of the melting point of the eutectic mixture on the content of the benzene homolog for ternary systems.

Table 5

Variable component in the homologous series with naphthalene (T_h, °C)*	Properties of the eutectic**	
	T_{eut}, °C	naphthalene content x, mol %
Propylbenzene (–99.5)	–101	1.5
Butylbenzene (–87.99)	–89	1.9
1-Butyl-4-methylbenzene (–85.0)	–85.7	2.1
1,3-Dimethyl-5-ethylbenzene (–84.33)	–85.0	2.2
1,3-Diethylbenzene (–83.92)	–84	2.2
Sec-butylbenzene (–75.49)	–76	2.6
1-Pentylbenzene (–75)	–75	2.7
1-Isopropyl-2-methylbenzene (–71.54)	–72	2.9
1-Isopropyl-4-methylbenzene (–67.94)	–68	3.1
1,2-Dimethyl-4-ethylbenzene (–67.0)	–67.5	3.2
1,3,5-Triethylbenzene (–66.5)	–67.0	3.2
1-Isopropyl-3-methylbenzene (–63.75)	–64	3.4
1,3-Diisopropylbenzene (–63.1)	–63.7	3.5
2,4-Dimethyl-1-ethylbenzene (–63.0)	–63.6	3.5
Tret-butylbenzene (–57.86)	–58	3.9
1,2-Diisopropylbenzene (–56.7)	–57	4.0
1,4-Dimethyl-1-ethylbenzene (–53.7)	–54	4.2
1-*Tret*-butyl-4-methylbenzene (–52.52)	–53	4.3
Isobutylbenzene (–51.52)	–52	4.4
1-*Tret*-butyl-2-methylbenzene (–50.32)	–51	4.5
1,2-Dimethyl-3-ethylbenzene (–49.5)	–50	4.6
1,4-Diethylbenzene (–42.85)	–44	5.3
1,2,4-Trimethylbenzene (–43.91)	–45	5.2
1,2,3-Trimethylbenzene (–25.38)	–28	7.6
1,2,3,5-Tetramethylbenzene (–23.69)	–27	7.8
1,3-Dimethyl-2-ethylbenzene (–16.3)	–21	9.0
1,2,3,4-Tetramethylbenzene (–6.25)	–12	10.9

* The melting points of the benzene homologs are taken from [3].

** Decimal values are shown only to illustrate the trends in the eutectic melting point and the content of the variable component in the homologous series in the eutectic with similar melting points of the benzene homologs.

Table 6

Component 1	Component 2	Component 3
Naphthalene–1,2-dimethylbenzene–benzene homologs		
Naphthalene	1,2-Dimethylbenzene	Butylbenzene (–87.99)
Naphthalene	1,2-Dimethylbenzene	1-Butyl-4-methylbenzene (–85.0)
Naphthalene	1,2-Dimethylbenzene	1,3-Dimethyl-5-ethylbenzene (–84.33)
Naphthalene	1,2-Dimethylbenzene	1,3-Diethylbenzene (–83.92)
Naphthalene	1,2-Dimethylbenzene	*Sec*-butylbenzene(–75.49)
Naphthalene	1,2-Dimethylbenzene	1-Pentylbenzene (–75)
Naphthalene	1,2-Dimethylbenzene	1-Isopropyl-2-methylbenzene (–71.54)
Naphthalene	1,2-Dimethylbenzene	1-Isopropyl-4-methylbenzene (–67.94)
Naphthalene	1,2-Dimethylbenzene	11,2-Dimethyl-4-ethylbenzene (–67.0)
Naphthalene	1,2-Dimethylbenzene	1,3,5-Triethylbenzene (–66.5)
Naphthalene	1,2-Dimethylbenzene	1-Isopropyl-3-methylbenzene (–63.75)
Naphthalene	1,2-Dimethylbenzene	1,3-Diisopropylbenzene (–63.1)
Naphthalene	1,2-Dimethylbenzene	2,4-Dimethyl-1-ethylbenzene (–63.0)
Naphthalene	1,2-Dimethylbenzene	*Tert*-butylbenzene (–57.86)
Naphthalene	1,2-Dimethylbenzene	1,2-Disiopropylbenzene (–56.7)
Naphthalene	1,2-Dimethylbenzene	1,4-Dimethyl-1-ethylbenzene (–53.7)
Naphthalene	1,2-Dimethylbenzene	1-*Tert*-butyl-4-methylbenzene (–52.52)
Naphthalene	1,2-Dimethylbenzene	Isobutylbenzene (–51.52)
Naphthalene	1,2-Dimethylbenzene	1-*Tert*-butyl-2-methylbenzene (–50.32)
Naphthalene	1,2-Dimethylbenzene	1,2-Dimethyl-3-ethylbenzene (–49.5)
Naphthalene–1,4-dimethylbenzene–benzene homologs		
Naphthalene	1,4-Dimethylbenzene	Butylbenzene (–87.99)
Naphthalene	1,4-Dimethylbenzene	1-Butyl-4-methylbenzene (–85.0)
Naphthalene	1,4-Dimethylbenzene	1,3-Dimethyl-5-ethylbenzene (–84.33)
Naphthalene	1,4-Dimethylbenzene	1,3-Diethylbenzene (–83.92)
Naphthalene	1,4-Dimethylbenzene	*Sec*-butylbenzene (–75.49)
Naphthalene	1,4-Dimethylbenzene	1-Pentylbenzene (–75)
Naphthalene	1,4-Dimethylbenzene	1-Isopropyl-2-methylbenzene(–71.54)
Naphthalene	1,4-Dimethylbenzene	1-Isopropyl-4-methylbenzene (–67.94)
Naphthalene	1,4-Dimethylbenzene	1,2-Dimethyl-4-ethylbenzene (–67.0)
Naphthalene	1,4-Dimethylbenzene	1,3,5-Triethylbenzene (–66.5)
Naphthalene	1,4-Dimethylbenzene	1-Isopropyl-3-methylbenzene (–63.75)
Naphthalene	1,4-Dimethylbenzene	1,3-Diisopropylbenzene (–63.1)
Naphthalene	1,4-Dimethylbenzene	2,4-Dimethyl-1-ethylbenzene(–63.0)
Naphthalene	1,4-Dimethylbenzene	*Tret*-butylbenzene (–57.86)
Naphthalene	1,4-Dimethylbenzene	1,2-Disiopropylbenzene (–56.7)
Naphthalene	1,4-Dimethylbenzene	1,4-Dimethyl-1-ethylbenzene (–53.7)
Naphthalene	1,4-Dimethylbenzene	1-*Tret*-butyl-4-methylbenzene(–52.52)
Naphthalene	1,4-Dimethylbenzene	Isobutylbenzene(–51.52)
Naphthalene	1,4-Dimethylbenzene	1-*Tret*-butyl-2-methylbenzene (–50.32)
Naphthalene	1,4-Dimethylbenzene	1,2-Dimethyl-3-ethylbenzene (–49.5)
Naphthalene	1,4-Dimethylbenzene	1,4-Diethylbenzene (–42.85)
Naphthalene	1,4-Dimethylbenzene	1,2,4-Trimethylbenzene(–43.91)
Naphthalene	1,4-Dimethylbenzene	1,2,3-Trimethylbenzene (–25.38)
Naphthalene	1,4-Dimethylbenzene	1,2,3,5-Tetramethylbenzene (–23.69)
Naphthalene	1,4-Dimethylbenzene	1,3-Dimethyl-2-ethylbenzene (–16.3)
Naphthalene	1,4-Dimethylbenzene	1,2,3,4-Tetramethylbenzene (–6.25)

Table 6. (Contd.)

Component 1	Component 2	Component 3
Naphthalene-1,2-dimethylbenzene– benzene homologs		
Naphthalene	Benzene	Butylbenzene (–87.99)
Naphthalene	Benzene	1-Butyl-4-methylbenzene (–85.0)
Naphthalene	Benzene	1,3-Dimethyl-5-ethylbenzene (–84.33)
Naphthalene	Benzene	1,3-Diethylbenzene (–83.92)
Naphthalene	Benzene	*Sec*-butylbenzene (–75.49)
Naphthalene	Benzene	1-Pentylbenzene (–75)
Naphthalene	Benzene	1-Isopropyl-2-methylbenzene (–71.54)
Naphthalene	Benzene	1-Isopropyl-4-methylbenzene(–67.94)
Naphthalene	Benzene	1,2-Dimethyl-4-ethylbenzene (–67.0)
Naphthalene	Benzene	1,3,5-Triethylbenzen (–66.5)
Naphthalene	Benzene	1-Isopropyl-3-methylbenzene (–63.75)
Naphthalene	Benzene	1,3-Diisopropylbenzene (–63.1)
Naphthalene	Benzene	2,4-Dimethyl-1-ethylbenzene(–63.0)
Naphthalene	Benzene	*Tret*-butylbenzene (–57.86)
Naphthalene	Benzene	1,2-Disiopropylbenzene (–56.7)
Naphthalene	Benzene	1,4-Dimethyl-1-ethylbenzene (–53.7)
Naphthalene	Benzene	1-*Tret*-butyl-4-methylbenzene (–52.52)
Naphthalene	Benzene	Isobutylbenzene (–51.52)
Naphthalene	Benzene	1-*Tret*-butyl-2-methylbenzene (–50.32)
Naphthalene	Benzene	1,4-Diethylbenzene (–42.85)
Naphthalene	Benzene	1,2,4-Trimethylbenzene (–43.91)

tal costs and permits the derivation of exhaustive information regarding the behavior of complex poly-eutectic systems.

CONCLUSIONS

(1) The variation in composition and melting point of eutectic mixtures in series of binary eutectics of thiophene and naphthalene with benzene homologs is established. The melting point of the eutectic mixtures increases with increase in melting point of the benzene homolog. With increase in the content of thiophene (the constant component of the series) in the eutectic mixture, its melting point increases. The same behavior is observed for series consisting of naphthalene + benzene homologs.

(2) We have predicted the existence of eutectics, their approximate melting points, and the composition of the eutectic mixtures for 21 binary systems of the series consisting of thiophene + benzene homologs and for 27 binary systems of the series consisting of naphthalene + benzene homologs. We have also obtained qualitative data regarding the presence of eutectics in 67 ternary systems formed by naphthalene with benzene homologs.

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